COATINGS. SEALS

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FORMATION OF LOW-TEMPERATURE SEALS AND COATINGS BASED ON LOW-MELTING LEAD-TELLURITE GLASSES

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The process of formation of seals and coatings based on low-melting lead-tellurite glasses is studied. The results of a microspectral analysis of the element distribution in glass – aluminum and glass – quartz seals are specified.

The development of vacuum-tight seals, passivation, and sealing of bodies of instruments remains a topical problem in the production of instruments. The trend of decreasing the weight and overall sizes of instruments calls for using such nontraditional materials, as aluminum, copper, and their alloys, as well as monocrystalline quartz and piezoquartz. This, in turn, makes it necessary to develop new sealing glass materials ensuring protection from corrosion, insulation, and airtightness of single microchips and of the instrument body.

Epoxy resins and organic adhesives used for the above purposes do not meet the requirements imposed on their strength, vacuum-tightness, and reliability; moreover, they are not moisture-resistant or heat-resistant. When a device has to operate under stringent conditions (enhanced humidity and high temperatures), such materials are totally unsuitable for sealing and passivating instruments. The most promising are inorganic glasses and glass cements, whose advantages over organic dielectrics include their moisture impermeability, strength, and their ability to withstand higher temperatures.

It is known that the process of adhesion of glass to metal proceeds in two stages. The first stage is glass wetting the metal surface. After the complete spreading of glass over metal and the manifestation of adhesion forces, the second stage starts: cohesion with the formation of a transition layer and modification of the concentration of the initial components near the interface. A strong adhesion of glass to metal is achieved due to the physiochemical interaction between the contacting phases leading to the formation of the transition layer.

An essential factor for obtaining a strong contact between glass and metal is a conformity between their CLTE [1]. Failure to meet this condition may lead to the seal breaking off, initiate cracks and other defects related to the mechanical disturbance of the integrity of the coating, and increase stresses in glass sealed to metal. If the CLTE of glass and metal are equal or little different, a compatible seal is formed.

The purpose of our study is to investigate the formation of low-temperature seals and vitreous coatings based on low-melting lead tellurite.

We have earlier synthesized low-melting lead-tellurite glasses in the four-component system $PbO – ZnO – B_2O_3 – TeO_2$ [2]. The evaluation of the melting and working properties of experimental glasses indicates that at 950°C an extensive range of clear glasses and glasses crystallizing under heat treatment is formed, which makes it possible to predict the compositions of both clear glass seals and glass-ceramic cements. As a consequence, compositions of low-melting lead-tellurite glasses were developed for seals and vitreous coatings to be applied to aluminum, monocrystalline quartz, and piezoquartz.

The developed low-melting glasses were used to produce low-temperature glass – aluminum, glass – monocrystalline quartz, and glass – piezoquartz seals.

The technology for producing seals and vitreous coating consists of the following operations: milling glass granulate to a specific surface area of 2500 cm^2/g, preparation of an aqueous suspension based on glass powder, and applying it to the substrate and forming a seal according to the developed time-temperature schedule.

The transition layer in the glass – aluminum and glass – quartz seals has been studied using x-ray-spectral microanalysis (MS-46 electron-probe microanalyzer produced by the Cameca Company). The studies were performed on thor-

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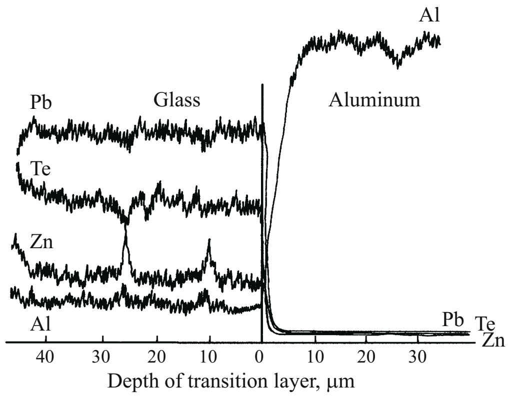

Fig. 1. Distribution of elements in glass – aluminum seal.

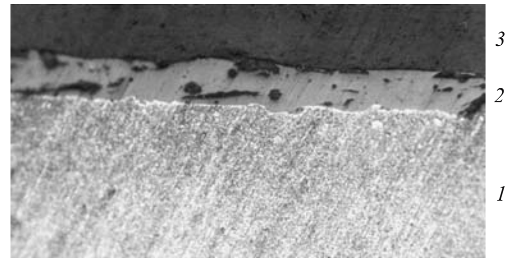

Fig. 2. Metallographic photo of glass – aluminum seal (× 200): *1*) aluminum substrate; *2*) transition layer; *3*) glass.

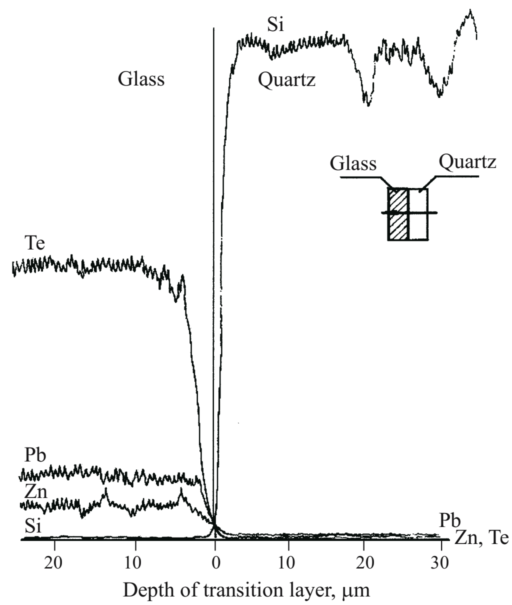

Fig. 3. Distribution of elements in glass – quartz seal.

oughly prepared sections with polished flat surfaces to preserve the topography and chemistry of the surface layer.

The results of x-ray spectral microanalysis of the element distribution in the glass- aluminum seal are shown in Fig. 1. An analysis of the spectral lines in the seal indicates that metal ions diffuse into the glass melt during sealing. The glass melt ions, in turn, diffuse into aluminum.

In the contact of metal with molten glass, a double electric layer is formed on the interface [3]. Usually metal is charged negatively, which is due to the oxidation of its surface and the transition of metal ions into the melt. The jump in the potential on the phase boundary facilitates the emergence of exchange currents between the metal and glass melt, which is manifested in the form of redox electrochemical reactions. A special role in this process belongs to variable-valence elements. The analyzed glasses contain lead oxides. Consequently, the lead ions in the melt, being variable-valence ions, activate the redox processes between the glass and aluminum.

The Al_2O_3 film formed on the metal impedes a deep penetration of the melt ions into aluminum, as a consequence they become concentrated on the surface of the metal. It is seen in Fig. 1 that the concentration distribution curves of Zn^{2+}, Te^{4+}, Pb^{2+} (Pb^{3+}) ions in aluminum are close to the zero mark. A sharp concentration transition is observed for all elements on the contact surface of the glass melt with aluminum, which is due to the different chemical compositions of the contacting materials and indicates the absence of a reaction zone between the glass and the metal. Apparently, the adhesion of glass to aluminum occurs due to redox and diffusion processes. The thickness of the transition layer formed between contacting phases is approximately 5 μm. In contrast to the glass melt ions, aluminum ions penetrate to a certain depth into the melt, therefore it can be supposed that the transition layer is formed on the side of the glass. A low sealing temperature (below 500°C) and a short exposure presumably prevent the sufficient development of the diffusion process and expansion of the contact zone.

It should be noted that the adhesion strength depends on the size of the transition layer. If its thickness is small, it is impossible to obtain a strong seal. A too thick transition layer has a low mechanical strength and can become a concentrator of dangerous stresses. In most metal-glass seals the optimum size of the transition layer should not exceed 5 – 10 μm.

Since the developed glass forms a strong bond to the aluminum substrate, it could be supposed that the thickness of the formed transition layer is sufficient for a strong seal between glass and aluminum. The formation of the transition layers in sealing glass to aluminum is corroborated by metallographic analysis. The metallographic photo (Fig. 2) exhibits a band between the glass – aluminum contacting phases, which can be interpreted as a transition layer.

It can be seen in Fig. 3 that the curves of the element distribution in the glass – quartz seal are somewhat different from such curves for the glass – aluminum seal. The elements of the contacting phases in glass (Zn^{2+}, Te^{4+}, Pb^{2+}) and quartz (Si^{4+}) are concentrated on the glass – quartz interface in the contact zone. In this case even if a transition layer is formed, its size is insignificant. The diffusion of silicon ions from monocrystalline quartz is impeded. In this case we

deal with the crystal – glass phase – melt system, where each component has a different diffusion coefficient and different process activation energy. The crystal of quartz, which typically has an ordered structure and a high strength of links at the crystal lattice points, has the lowest diffusion coefficient and the maximum diffusion activation energy compared with glass. Considering that diffusion is a thermally activated process requiring a high temperature and a long exposure to be started in a crystalline material [4], it can be assumed that diffusion processes in the glass – quartz monocrystal heterophase system at a low sealing temperature (below 500°C) take place mainly due to the low-melting glass. Consequently, a strong adhesion of glass to monocrystalline quartz is presumably achieved due to contact melting.

Thus, the formation of a strong seal between glass and aluminum occurs as a result of redox and diffusion process accompanied by the formation of a transition layer. The glass-quartz seal is presumably formed as a consequence of contact melting.

At present low-melting lead-tellurite glasses are used as sealing coatings and seals with monocrystal quartz and piezoquartz in the production of sensors, in particular, in barosensitive and thermosensitive quartz resonators and accelerometers produced at the SKTB ElPA Company (town of Uglich).

The developed glasses can be used for passivation and also for seals and sealing coatings in the production of microchips and integrals circuits on aluminum substrates.

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